Environmental Conditions Controlling Selenium Volatilization from a Wetland System

YIQIANG ZHANG* AND
JOHNNIE N. MOORE

Department of Geology, University of Montana, Missoula, Montana 59812

Natural selenium volatilization from Benton Lake, MT, a wetland system containing moderate levels of selenium, was studied in water−sediment, water−sediment with a flooding−drying cycle, and plant−water−sediment microcosms. Results showed that selenium volatilization occurred from water, sediment, and wetland plants. Sediment and plants were the major producers of volatile selenium from the system. The rate of selenium volatilization from algae and high-selenium sediment was much higher than that from watermilfoil and low-selenium sediment. The rate was also controlled by various environmental factors. Higher temperature, higher air flow, flooding−drying and the decomposition of wetland plants greatly increased the removal rates of selenium through selenium volatilization. Our results suggest that natural selenium volatilization can be an important process removing selenium from wetland systems.

Introduction

Selenium accumulation is occurring in many wetlands of the western United States (*1, 2*). Although there are no documented deleterious effects on waterfowl in most of these wetlands, selenium concentrations may continue to rise and will pose a threat to wildlife in the future. Cooke and Bruland (*3*) estimated that about 30% of the selenium entering a wetland is removed through natural selenium volatilization. If this natural selenium volatilization can be enhanced through active wetland management, it would provide an economical and effective method for reducing selenium accumulation to minimize the hazard from selenium to waterfowl.

Selenium volatilization is considered to be an effective technique for removing selenium from selenium-contaminated sites (*4*). The rates of selenium volatilization are dependent on the selenium species present, microbial activity, and various environmental conditions (*5−18*). Selenium volatilization studies have been carried out in water (*15−17*), plants (*13, 14, 19*), soils (*9−11*), and sediments (*5−8, 12*), providing valuable information on the spatial and temporal dynamics of selenium volatilization in natural systems. Less attention has been paid to selenium volatilization from wetlands containing moderate levels of selenium and containing a complex mosaic of water, sediment, and plants.

Selenium accumulation in a wetland system is controlled by selenium inputs and organic matter content in each pond and the management of the pond system (*20*). Changes and adjustments of current wetland management—for example, water flow within the lake and the rotation of perennial- and seasonally-flooded ponds—could change the degree and dominance of different biogeochemical processes and thus

TABLE 1. Total Dissolved Selenium and Dissolved Organic Selenium (in Parentheses) Concentrations in Water (μg/L) and Total Selenium in Sediment and Plants (μg/g) in Microcosms at the Beginning of Experiments

samples	microcosm 1	microcosm 2
Water		
WS[a] (11/2/1994)	2.39 (1.18)	1.61 (0.96)
WS[a] with flooding−drying cycling (6/4/1995)	2.99 (2.47)	2.92 (2.30)
PWS[b] (9/13/1995)	2.84 (0.71)	8.22 (6.47)
Sediment		
WS[a] (11/2/1994)	7.43	1.15
Plants		
watermilfoil	3.71	
algae		4.92

[a] Water−sediment system. [b] Plant−water−sediment system.

affect the rates of selenium accumulation and volatilization. Therefore, information about selenium volatilization in wetland systems is very important to managers of these wetlands. The objective of this study is to determine the rates of selenium volatilization under different environmental conditions and to provide information on processes and conditions affecting those rates. Selenium volatilization was studied in laboratory microcosms. In order to simulate natural wetland conditions, water−sediment, water−sediment with a flooding−drying cycle, and plant−water−sediment systems were used. The effects of varying dissolved selenium concentrations, temperature, air flow rates, time, algae concentration, and decomposition of plants on selenium volatilization were also examined.

Materials and Methods

Samples (Table 1) used for studying selenium volatilization were collected in 1994−1995 from Benton Lake, MT (*20, 21*), a wetland system with moderate selenium levels typical of western United States wildlife refuges contaminated with selenium (*1*). Water and sediment were collected from two sites: one with relatively high concentration of sediment selenium (7.43 μg/g), termed "high-selenium" (used in microcosm 1, Table 1), and another from a site with relatively low concentration of sediment selenium (1.15 μg/g), termed "low-selenium" (used in microcosm 2, Table 1). Microcosms were constructed by placing about 7.5 L of wetland sediment and about 7.9 L of overlying water in a semitransparent plastic tub (38 × 25 × 22 cm). The microcosms were kept at room temperature until a very thin oxidized layer formed on the surface of the sediment—the situation seen in the field. Then, another semitransparent plastic tub (38 × 25 × 14 cm) with a small air inlet hole and an activated-carbon column (made by packing activated carbon in a 10-mL syringe) attached to an outlet hole was placed upside down on, and sealed with plastic tap to, each tub (Figure 1). Selenium gases produced in the microcosms were pulled into the activated-carbon column and adsorbed on the activated carbon surface (*12*) by using a small vacuum pump (producing an air flow of 0.8 L/min to the outlet).

Rates of selenium volatilization were examined in three different experiments in microcosms 1 and 2 in a temperature-controlled room where temperature was maintained within ±0.5 °C. In the first experiment (from November 1994 to March 1995), a water−sediment system was used to examine the effects of concentration of dissolved selenium and sediment selenium and temperature on the rate of selenium volatilization. This experiment was designed to be a four-
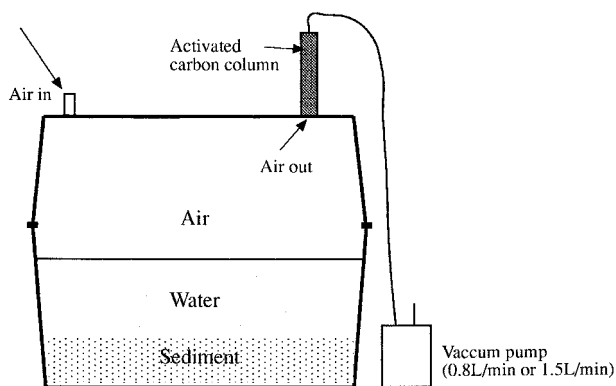
FIGURE 1. Apparatus for collecting volatile selenium from water—sediment system.

step process (Figure 2). Each step was begun by adding a volume (12.5, 10, 10, and 10 mL, respectively, for the four steps) of a solution with known selenium concentration (0.271 mg/L selenite, 23.0 mg/L selenate, and 2.13 mg/L organic selenium). Temperature of the water in the microcosms was monitored with a thermometer. Temperature was maintained at 19 °C in the first and second steps (Figure 2B). Beginning with step 3, the temperature was reduced to 8.5 °C followed by an increase to 30.5 °C. Step 4 was begun at 30.5 °C followed by a decrease to 4 °C. Water and volatile selenium were sampled at 1—4-day intervals for a period of 123 days. Dissolved oxygen and pH in the water were determined using a dissolved oxygen meter (Orion 820) and a pH meter (Orion 290A) weekly or biweekly.

The second experiment (from June to September 1995) determined the effects of a flooding—drying cycle on selenium volatilization in the water—sediment system. At the start of this experiment (Figure 3), water from Benton Lake was added to the microcosms to cover the sediment to simulate a flooding condition. After 8 days, water was removed from the microcosms, and the sediment was exposed to the air. Moisture evaporated from surface sediment was pumped out to simulate a drying process. After 76 days of drying, water
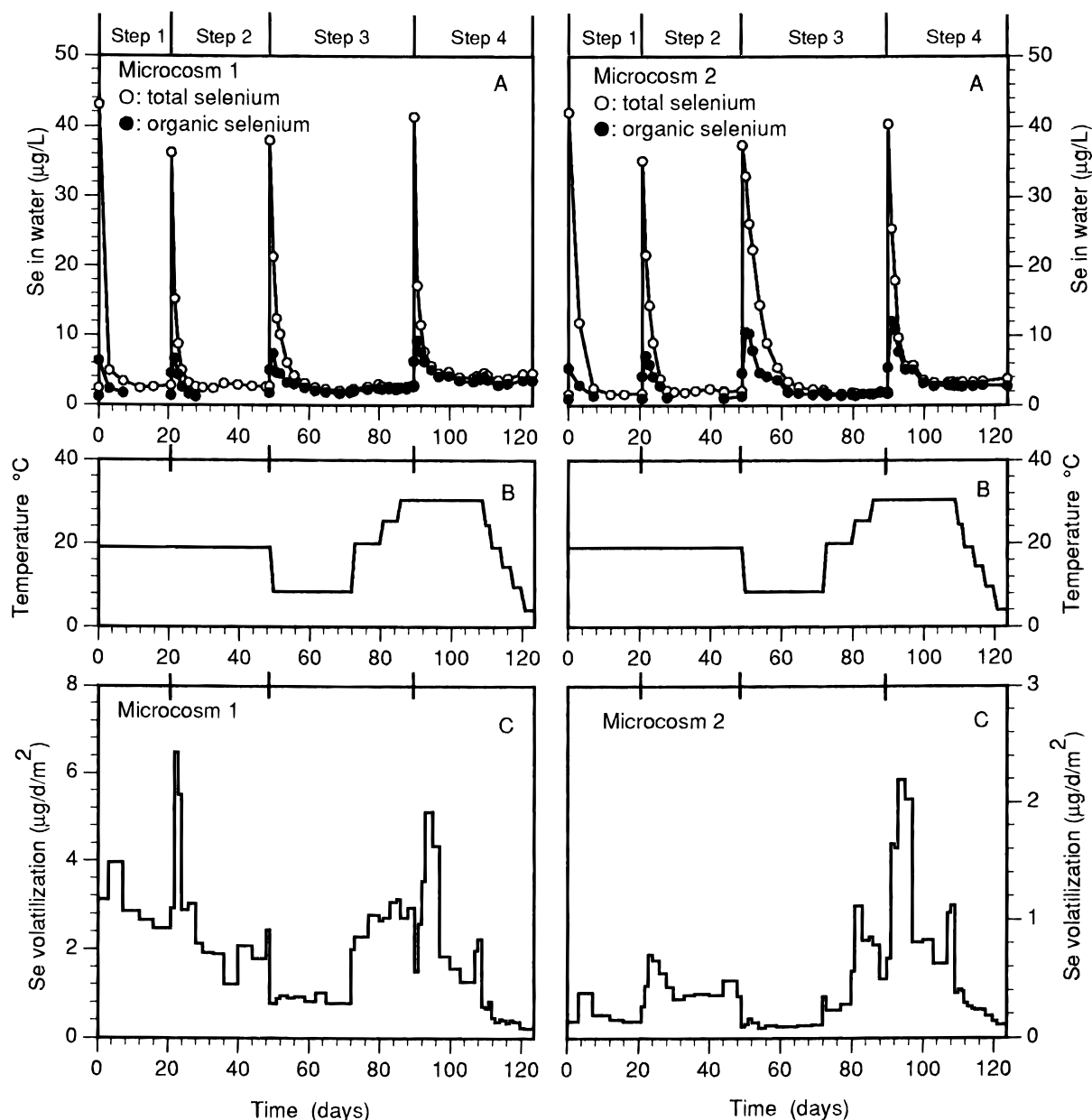

FIGURE 2. Relationship between volatilization rate of selenium from water—sediment system and temperature, and concentration of total dissolved selenium and dissolved organic selenium: (A) changes of concentration of total dissolved selenium and dissolved organic selenium with time; (B) changes of temperature with time; (C) changes of volatilization rate with time.
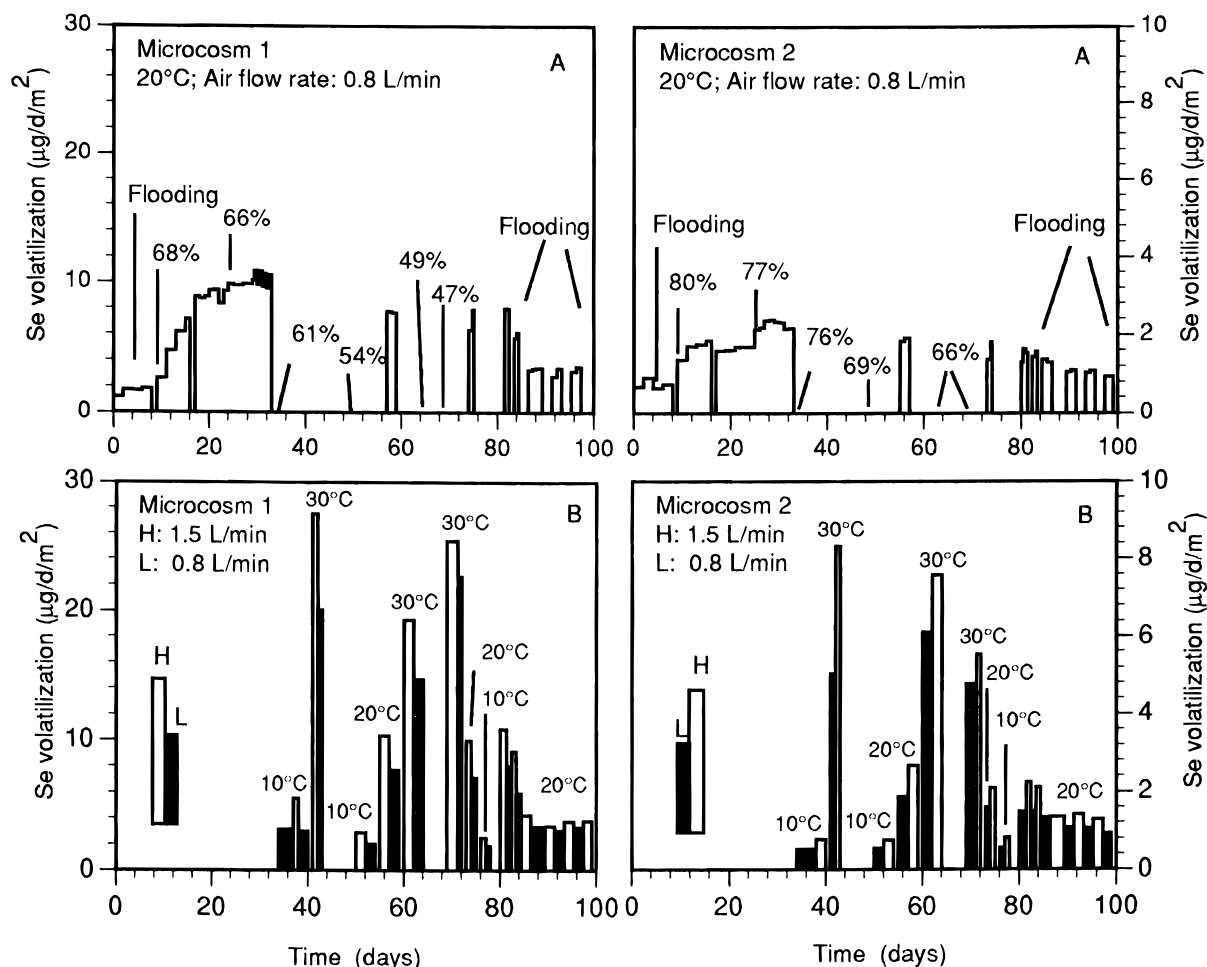
FIGURE 3. Selenium volatilization from a water—sediment system with flooding—drying—flooding cycle: (A) selenium volatilization at 20 °C with a low air flow rate (0.8 L/min), percent data show water percent in surface sediment; (B) selenium volatilization at different temperatures with different air flow rates (a mean of duplicate or triplicate values was used).

collected from Benton Lake was again added to the microcosms to simulate another flooding condition. In this experiment, the effects of temperature, water content in surface sediment, and air flow rate on selenium volatilization were examined. Temperature was adjusted from 10 to 30 °C in 10 °C steps (Figure 3B). Moisture content was monitored by measuring percent water in surface sediment. Two different vacuum pumps were used to periodically change air flow rates (0.8 and 1.5 L/min, Figure 3B). Volatile selenium was sampled at 3-h to 1-day intervals for a period of 99 days.

The third experiment (from September to October 1995) determined the effect of algae and decomposition of watermilfoil on selenium volatilization in plant—water—sediment systems. Watermilfoil and algae were collected from Benton Lake in 1995 (Table 1)—their species were not determined. Selenium concentration was 3.71 μg/g in watermilfoil and 4.92 μg/g in algae. After sampling, watermilfoil (500 g wet weight) was added to microcosm 1 to make a watermilfoil—water—sediment system (WWS), and algae (500 g wet weight) were added to microcosm 2 to make an algae—water—sediment microcosm (AWS). In order to compare results from WWS and AWS systems, selenium volatilization directly from watermilfoil (500 g wet weight) and algae (500 g wet weight) were also studied in other algae and watermilfoil microcosms. These two microcosms were made by adding watermilfoil and algae to devices similar to microcosms 1 and 2 described above. During this experiment, the effect of temperature on selenium volatilization was examined by adjusting temperature ranging from 10 to 30 °C (Table 5; Figure 4). Water samples in WWS and AWS were collected five times during the experiment to determine concentration of total dissolved

selenium and dissolved organic selenium (Table 4). Volatile selenium from this third experiment was sampled at 3-h to 1-day intervals for a period of 14 days.

Total selenium concentrations in sediment, watermilfoil, and algae were determined using a hydrogen peroxide—hydrochloric acid digestion procedure (20). Selenium speciation in water samples was determined using an XAD—resin separation method (22). Volatile selenium in the activated carbon column was measured using a methanol desorption method (12). Selenium concentrations in all samples were determined using continuous-flow hydride-generation atomic absorption spectrometry (20). Water content in surface sediment was determined by calculating the loss in weight after drying samples at 75 °C. All concentrations of selenium in sediment and plants were expressed on a 75 °C dry-sample basis.

Results

Selenium Volatilization from Water—Sediment System. During the experiment, pH was about 8.5 in water, and dissolved oxygen concentrations were about 1.0—2.0 mg/L on the water surface and 0—0.2 mg/L at the sediment—water interface. The rate of selenium volatilization from the water—sediment system was related to selenium concentrations in the water (Figure 2). At the beginning of each step of the four steps of the experiment, concentrations of total dissolved selenium in both microcosms were high, ranging from 35 to 43 μg/L and then decreased with time to about 1.6—4.0 μg/L. At the beginning of each step, concentrations of dissolved organic selenium ranged from 4.19 to 6.34 μg/L, made up
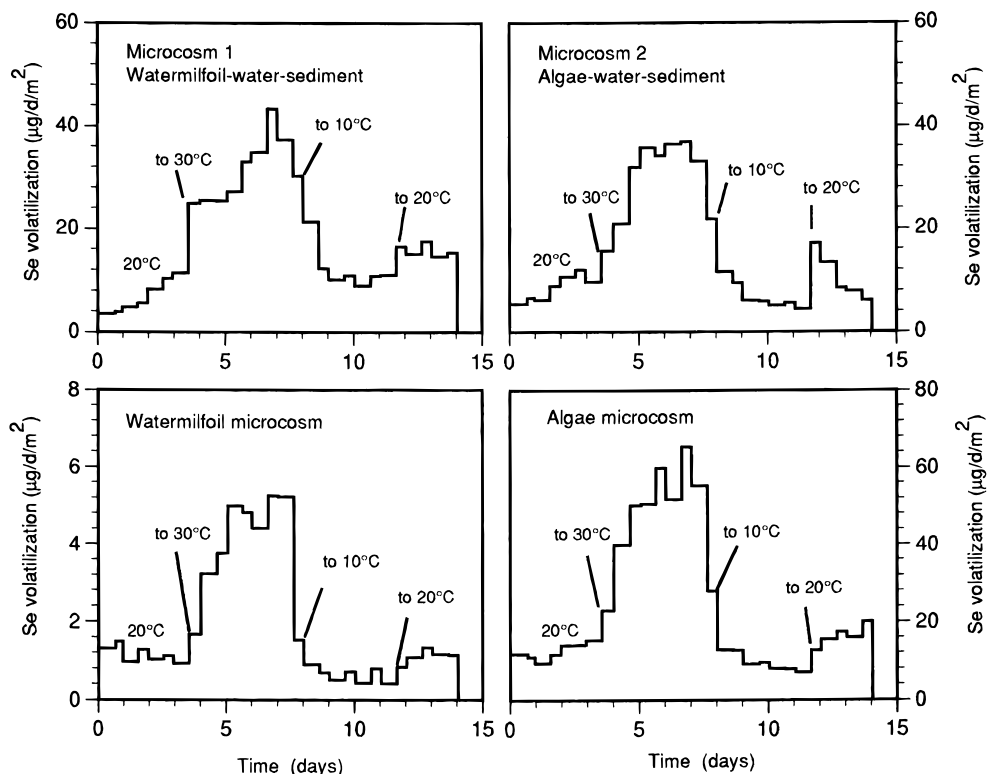
FIGURE 4. Selenium volatilization from watermilfoil alone, watermilfoil—water—sediment, algae alone, and algae—water—sediment systems.

12.6—15.3% of the total dissolved selenium, and then (2—4 steps) increased to maximum values after 1 day of experiment. After that, concentration of dissolved organic selenium with time decreased to about 1.0 to 4.0 μg/L and made up 46—98% of the total dissolved selenium. During the first 1—3 days of each step of the experiment, the rate of selenium volatilization was relatively low. It then increased to a maximum in both microcosms at 2—3 days and then decreased following the concentrations of total dissolved selenium and dissolved organic selenium. Only in step 3, at low temperature, was this response muted.

The rate of selenium volatilization was also related to the initial selenium concentrations in the sediment (Figure 2). During the four steps of the experiment, water concentration of selenium was very similar in both microcosms at each sampling time. However, the rate of selenium volatilization from microcosm 1 (high-selenium sediment) was much higher than that from microcosm 2 (low-selenium sediment). The difference in the rates of selenium volatilization between the two microcosms showed a general decreasing trend with each step of the experiment. The average rate in microcosm 1 was about 14 times higher than that in microcosm 2 in the first step of the experiment, about 5—6 times higher in the second and the third steps, and about 1 time higher in the fourth step.

During these four steps of the experiment (123 days), the total amount of selenium volatilized was 244 μg/m^2 from microcosm 1 and 54 μg/m^2 from microcosm 2. Besides selenium concentrations in water and sediment, temperature also affected selenium volatilization from the water—sediment system in both microcosms with similar selenium concentrations in water (Figure 2; Table 2). In the first 7 days, when selenium concentration in water was relatively high in each step, the average rate of selenium volatilization in both microcosms was lower at 8.5 °C than at 30.5 °C. In microcosm 1, volatilization rates changed from 0.88 μg d^{-1} m^{-2} at 8.5 °C to 3.8 μg d^{-1} m^{-2} at 30.5 °C from step 3 to step 4. In microcosm 2, volatilization rates changed from 0.166 μg d^{-1} m^{-2} at 8.5 °C to 1.77 μg d^{-1} m^{-2} at 30.5 °C from step 3 to step 4. After 7 days, when water concentrations of selenium were relatively

TABLE 2. Rates (μg d^{-1} m^{-2}) of Selenium Volatilization from Water—Sediment System at Different Temperatures

	microcosm 1		microcosm 2	
temp steps	first 7 days[a]	after 7 days[b]	first 7 days[a]	after 7 days[b]
first (19 °C)	3.60	2.66	0.279	0.163
second (19 °C)	3.84	1.84	0.547	0.378
third (8.5 °C)	0.88	0.86	0.116	0.105
fourth (30.5 °C)	3.80	1.63	1.767	0.802

[a] Water concentrations of selenium were high at the first 7 days.
[b] Water concentrations of selenium were low after 7 days.

low, the average rate of selenium volatilization decreased in both microcosms over the same temperature step. In microcosm 1, volatilization rates increased from 0.86 μg d^{-1} m^{-2} at 8.5 °C to 1.63 μg d^{-1} m^{-2} at 30.5 °C from step 3 to step 4 and in microcosm 2 from 0.105 μg d^{-1} m^{-2} at 8.5 °C to 0.802 μg d^{-1} m^{-2} at 30.5 °C from step 3 to step 4. After 108 days during step 4, when the temperature was decreased from 30.5 to 4.0 °C and the selenium concentration in water was low, the volatilization rate decreased in both microcosms. Volatilization rates changed from 2.24 to 0.222 μg d^{-1} m^{-2} in microcosm 1 and from 1.12 to 0.113 μg d^{-1} m^{-2} in microcosm 2.

Selenium Volatilization from Water—Sediment System with a Flooding—Drying-Flooding Cycle. At the beginning of this experiment in a flooding condition, water concentrations of selenium were 2.99 μg/L in microcosm 1 and 2.92 μg/L in microcosm 2 (Figure 3; Table 1). The rate of selenium volatilization with a low air flow rate at 20 °C was low under the flooded condition (Figure 3A). After 8 days, the rate of selenium volatilization increased with dewatering of the sediment when water was removed from the microcosms. After about 18 days, the volatilization rate stabilized. The flooding condition was re-established after 80 days by adding field water to the microcosms to form a very thin layer of water, then increased to about 0.5 cm (after 83 days), and then to 5 cm (after 88 days). The rate of selenium volatilization

TABLE 3. Rates (μg d^{-1} m^{-2}) of Selenium Volatilization from Dewatering Sediment at Different Temperatures and Air Flow Rates

	microcosm 1		microcosm 2	
temp (°C)	1.5 L/min	0.8 L/min	1.5 L/min	0.8 L/min
10	2.52−5.55	1.87−3.01	0.76−0.82	0.53−0.56
20	9.96−10.4	7.10−7.70	2.09−2.67	1.59−1.88
30	19.3−27.5	14.7−22.6	5.52−8.31	4.78−6.09

TABLE 4. Concentrations (μg/L) of Total Dissolved Selenium and Dissolved Organic Selenium (in Parentheses) in Plant−Water−Sediment System

sampling time	WWS[a]	AWS[b]
day 1	2.84 (0.71)	8.22 (6.47)
day 3	4.07 (3.04)	6.81 (5.76)
day 5	11.6 (10.0)	7.92 (6.37)
day 8	7.66 (4.96)	8.89 (5.92)
day 14	7.72 (7.00)	5.39 (3.39)

[a] Watermilfoil−water−sediment microcosm. [b] Algae−water−sediment microcosm.

TABLE 5. Rates (μg d^{-1} m^{-2}) of Selenium Volatilization from Plant and Plant−Water−Sediment

temp step[a] (°C)	WMF[b]	WWS[c]	algae	AWS[d]
20	0.93−1.49	3.55−11.4	9.40−15.4	5.35−12.0
20−30	1.68−3.22	24.9−25.5	22.9−39.8	15.6−21.0
30	3.75−5.25	25.4−43.3	50.1−65.4	31.9−36.9
30−10	0.69−1.53	12.2−30.2	12.7−28.0	9.41−21.9
10	0.41−0.72	8.93−11.0	7.04−9.17	4.42−6.12
10−20	0.84−1.09	15.0−16.5	12.6−15.5	13.4−17.0
20	1.14−1.33	14.6−17.5	15.9−20.1	6.08−8.41

[a] The order of temperature changes during experiment. [b] Watermilfoil. [c] Watermilfoil−water−sediment microcosm. [d] Algae−water−sediment microcosm.

decreased after flooding from 8.01 μg d^{-1} m^{-2} (81 days) to 5.73 μg d^{-1} m^{-2} (83 days) and finally to 3.5 μg d^{-1} m^{-2} (96 days) in microcosm 1 and from 1.64 μg d^{-1} m^{-2} (80 days) to 1.44 μg d^{-1} m^{-2} (82 days) and finally to 0.93 μg d^{-1} m^{-2} (97 days) in microcosm 2. During this experiment, the rate of selenium volatilization from microcosm 1 (high-selenium sediment) was about 1−2 times higher than those from microcosm 2 (low-selenium sediment) under flooding conditions and 3−4 times higher during drying.

The rate of selenium volatilization was also related to temperature and air flow rate (Figure 3B; Table 3). During drying of the surface sediment with different air flow rates (0.8 and 1.5 L/min), the average rates of selenium volatilization in both microcosms decreased with lowered temperature. In microcosm 1, volatilization rates changed from 27.5 to 5.55 μg d^{-1} m^{-2} at 30 and 10 °C, respectively. In microcosm 2, volatilization rates decreased from 4.78 to 0.53 μg d^{-1} m^{-2} over the same temperature range. During this experiment, the rate of selenium volatilization at 1.5 L/min air flow was about 40% higher than that at 0.8 L/min air flow during sediment drying.

Sediment selenium concentration also affected volatilization rate. The rate of selenium volatilization from microcosm 1 (high-selenium sediment) was about 3 times higher than that from microcosm 2 (low-selenium sediment). During the flooding−drying−flooding cycle in the water−sediment system over the entire 99 days of the experiment, the total amount of selenium volatilized was 561 μg/m^2 from microcosm 1 and 149 μg/m^2 from microcosm 2.

Selenium Volatilization from Plant−Water−Sediment System. Selenium volatilization from the two plant−water−sediment systems and from just plants was quite different (Figure 4; Table 5). In the WWS, decomposition of watermilfoil during the experiment decreased the amount of added watermilfoil, resulting in a significant increase of dissolved organic selenium concentration (Table 4) and a change to slightly yellow-colored water. At the beginning of this experiment at 20 °C, when concentrations of total dissolved selenium and dissolved organic selenium were low (Table 4), the rate of selenium volatilization was low (3.55 μg d^{-1} m^{-2}, Figure 4; Table 5). The rate of selenium volatilization increased slightly with time as the concentration of total dissolved selenium and dissolved organic selenium increased. After 4 days, when temperature was adjusted to 30 °C, concentration of total dissolved selenium and dissolved organic selenium increased to 11.6 and 10.0 μg/L, respectively,

and the rate of selenium volatilization increased rapidly. After 8 days, concentrations of dissolved selenium and dissolved organic selenium were 7.66 and 4.96 μg/L, respectively, and the rate of selenium volatilization was 30.2 μg d^{-1} m^{-2}. After 8.5 days, temperature was adjusted to 10 °C, and the rate of selenium volatilization deceased to 8.93 μg d^{-1} m^{-2}. After 12 days, as temperature was adjusted to 20 °C, the rate of selenium volatilization increased. On the final day (14 days) of this experiment, the rate of selenium volatilization was 15.3 μg d^{-1} m^{-2}, and concentrations of total dissolved selenium and dissolved organic selenium were 7.72 and 7.0 μg/L, respectively. In the watermilfoil microcosm at 20 °C (Figure 4; Table 5), the rate of selenium volatilization initially slightly decreased. As temperature was adjusted to 30 °C, then to 10 °C, and finally to 20 °C, the rates of selenium volatilization followed temperature: a large increase, a large decrease, and then a slight increase. During this 14-day experiment, the rate of selenium volatilization from the WWS was about 8 times higher than that from just watermilfoil. The maximum rate of selenium volatilization at 30 °C was 43.3 μg d^{-1} m^{-2} from the WWS and 5.25 μg d^{-1} m^{-2} from watermilfoil alone. The total amount of volatile selenium was 26.4 μg/m^2 from the watermilfoil alone experiment and 243 μg/m^2 from the WWS experiment.

In the AWS microcosm at 20 °C (Figure 4; Tables 4 and 5), initially concentrations of total dissolved selenium and dissolved organic selenium were 8.22 and 6.47 μg/L, and the rate of selenium volatilization was low (5.35 μg d^{-1} m^{-2}) and then slightly increased with time. After 4 days, when temperature was adjusted to 30 °C, concentrations of total dissolved selenium and dissolved organic selenium were 6.81 and 5.76 μg/L, respectively, and the rate of selenium volatilization increased rapidly. After 8 days, concentrations of dissolved selenium and dissolved organic selenium were 7.92 and 6.37 μg/L, respectively, and the rate of selenium volatilization was 21.8 μg d^{-1} m^{-2}. After 8.5 days, temperature was adjusted to 10 °C, and the rate of selenium volatilization deceased to 4.42 μg d^{-1} m^{-2}. After 12 days, as temperature was adjusted to 20 °C, the rate of selenium volatilization increased. On the final day (14 days) of this experiment, the rate of volatilization was 6.08 μg d^{-1} m^{-2}, and concentrations of total dissolved selenium and dissolved organic selenium were 5.39 and 3.39 μg/L, respectively. In the algae microcosm at 20 °C (Figure 4; Table 5), the rate of selenium volatilization during the first two days was low and then slightly increased with time. As temperature was adjusted to 30 °C, then to 10 °C, and finally to 20 °C, the rates in the algae microcosm followed temperature: a large increase, a large decrease, and then a slight increase. During this 14-day experiment, the rate of selenium volatilization from just algae was about 50% higher than that from the AWS. The maximum rate of selenium volatilization at 30 °C was 65.4 μg d^{-1} m^{-2} from algae and 36.4 μg d^{-1} m^{-2} from AWS. The total amount of volatile selenium was 326 μg/m^2 from the algae alone experiment and 211 μg/m^2 from AWS experiment.

Discussion

Selenium volatilization is an important biogeochemical process responsible for removing selenium from wetlands. It is a microbially mediated process (11, 23) that is affected by various environmental conditions. Those conditions include selenium concentration in water, sediment, and plants; flooding—drying of ponds; temperature; air flow; and decomposition of plants and organic materials.

Concentration of total dissolved selenium affects selenium volatilization in wetlands (17, 24) and the rate of selenium volatilization increases with the concentration of total dissolved selenium (17). Our results show a complex relationship between selenium volatilization rate and concentrations of total dissolved selenium. Initially, selenium volatilization rates did not show a positive relation to the concentration of total dissolved selenium. Volatilization rates were relatively low for the first few days of the experiment even when relatively high levels of dissolved selenium were added to the microcosms. After 1—3 days, however, volatilization rates increased to maximum values as selenium concentration in the water decreased rapidly. Then, volatilization rate was positively related to the total dissolved selenium concentrations. The mechanism causing this lag time is not known. One explanation might be microbially related—it takes time for microorganisms to respond to the increased amount of available selenium. The other is physical—a certain amount of volatile selenium must be formed before emission into the atmosphere because of the high solubility of volatile selenium (25).

Concentration of dissolved organic selenium is a more important factor affecting selenium volatilization than dissolved inorganic selenium (24). Cooke and Bruland (3) and Zayed and Terry (26) proposed pathways for the production of demethylselenide (DMSe), a dominant form of volatile selenium (3, 27), showing that organic selenium can directly transfer to volatile DMSe. Inorganic selenium needs to be first assimilated to organic selenium before forming DMSe. Therefore, formation of DMSe from organic selenium is easier than from inorganic selenium, and the rate of selenium volatilization is much higher in water containing organic selenium than that in water containing inorganic selenium (24). In this study, the rate of selenium volatilization was positively related to the concentration of dissolved organic selenium except during an initial lag time, similar to that seen for total dissolved selenium. Even when concentrations of total dissolved selenium and dissolved organic selenium were very low (Figure 2), the higher percentages of dissolved organic selenium in water—sediment system still caused volatile selenium emission to the atmosphere. In the plant—water—sediment system, the decomposition of watermilfoil significantly increased concentration of dissolved organic selenium, which likely resulted in a significant increase in the rate of selenium volatilization.

The rate of selenium volatilization is also positively related to the selenium concentration in sediment (5, 12). This results from the higher levels of dissolved selenate, selenite, and dissolved organic selenium in the high-selenium sediment (21) that are easily attacked by microorganism to form volatile selenium (11, 23). In this study, the volatilization rate of selenium from the high-selenium sediment was much higher than that from the low-selenium sediment in the water—sediment system containing similar water concentrations of selenium. In the dewatering sediment experiment, the rate of selenium volatilization from the high-selenium sediment was about 3—4 times higher than that from the low-selenium sediment. These results indicate that most of the volatile selenium emitted from the microcosms is mainly produced from the sediment.

Selenium volatilization by plants is considered to be an important process for removing selenium from selenium-contaminated sites (14). The rate of selenium volatilization from soil with barley and native salt grass was 19.6 and 6.9 times higher than that from just soil, respectively (28). Selenium volatilization also occurred in wetland plants (algae and watermilfoil) in this study. The rate of selenium volatilization was higher in algae alone than in watermilfoil alone. Addition of algae to the water—sediment microcosm substantially increased the rate of selenium volatilization—about 10 times higher than that from the water—sediment system alone. In contrast, the rate of selenium volatilization from the algae—water—sediment system was less than that observed from algae alone although there was a relatively high concentration of dissolved organic selenium in the algae—water—sediment system. This might be caused by a layer of algae on the water surface, which blocked volatile selenium emission from the water and sediment or assimilation of volatile dissolved selenium by the algae.

Transferring from a flooded condition to a drying condition in a wetland can greatly increase selenium volatilization. During the flooded condition, dissolved oxygen concentrations were low in the sediment surface, so selenium was likely in a reduced form and was less available to form volatile selenium. Part of the volatile selenium formed could also remain in the water due to the high solubility of volatile selenium (25). During drying, aerobic dewatering of sediment most likely causes decomposition of solid organic materials and selenium oxidation in surface sediment that releases dissolved organic and inorganic selenium. These selenium forms are readily available for forming volatile selenium (11, 23, 24), which can move directly into the atmosphere because there is little water for volatile selenium to dissolve into. In this study, the rate of selenium volatilization from exposed, dewatering sediment was higher than that from a flooded water—sediment system.

Selenium volatilization was substantially affected by the changes in temperature in the wetland microcosms. The volatilization rate from water, sediment and soil greatly increases with increased temperature (6, 16). In this study, the rate of volatilization was greater at high temperature than at low temperature in the water—sediment system. During sediment dewatering, the volatilization rate at 30 °C was about 2 times higher than that at 20 °C and 8 times higher than that at 10 °C.

The wind flow over a wetland is clearly a factor affecting selenium volatilization. Zieve and Peterson (29) found that volatile selenium can be adsorbed by soils so that high wind flow can rapidly remove volatile selenium from on and/or above the sediment surface, thus increasing selenium volatilization rate. In this study, increased air flow from 0.8 to 1.5 L/min resulted in increased selenium volatilization.

Decomposition of wetland plants greatly enhances selenium volatilization because plant decomposition can provide the methyl group (an important part of volatile selenium—dimethyselenide) and serves as a carbon source to stimulate microbial growth (5, 6, 9, 11, 12, 15, 16). This was confirmed by a study (15) in which the amount of volatile selenium was about 20-fold higher in a water—sediment system amended with organic carbon than that in an unamended system. In this study, the decomposition of watermilfoil significantly increased the rate of selenium volatilization, resulting in much higher rates than in the water—sediment system or just from watermilfoil. In comparison with the sum of volatilization rates from watermilfoil alone and the water—sediment system, the volatilization rate was still higher in the watermilfoil—water—sediment system. These results indicate that the decomposition of watermilfoil in the water—sediment system greatly increases the rate of selenium volatilization.

Wetlands are a complex system containing water, sediment, and a variety of organisms. These systems can produce and emit volatile selenium to the atmosphere, thus reducing selenium toxicity to wetland biota. Selenium in wetlands originates from weathered selenium-containing rocks and

may have somewhat different bioavailability for volatilization compared to the 'spike' that we added to the microcosms. Thompson-Eagle and Frankenberger (*15*) found that the rate of selenium volatilization measured in the field is about 1.7 times higher than that found in laboratory experiments. Therefore, to fully characterize selenium volatilization in a natural system, it is necessary to measure selenium volatilization in the field to calibrate and correct rates from laboratory studies. Even with this caveat, our results show that natural selenium volatilization can be an important process removing selenium from wetland systems.

Acknowledgments

Literature Cited

(1) Presser, T. S.; Sylvester, M. A.; Low, W. H. *Environ. Manage.* **1994**, *18*, 423−436.

(2) Presser, T. S. *Environ. Manage.* **1994**, *18*, 437−454.

(3) Cooke, T. D.; Bruland, K. W. *Environ. Sci. Technol.* **1987**, *21*, 1214−1219.

(4) Thompson-Eagle, E. T.; Frankenberger, W. T., Jr. *Adv. Soil Sci.* **1992**, *17*, 261−310.

(5) Calderone, S. J.; Frankenberger, W. T., Jr.; Parker, D. R.; Karlson, U. *Soil Biol. Biochem.* **1990**, *22*, 615−620.

(6) Frankenberger, W. T., Jr.; Karlson, U. *Soil Sci. Soc. Am. J.* **1989**, *53*, 1435−1442.

(7) Frankenberger, W. T., Jr.; Karlson, U. *Geomicrobiol. J.* **1994**, *12*, 265−278.

(8) Frankenberger, W. T., Jr.; Karlson, U. *J. Ind. Microbiol.* **1995**, *14*, 226−232.

(9) Karlson, U.; Frankenberger, W. T., Jr. *Soil Sci. Soc. Am. J.* **1988**, *52*, 1640−1644.

(10) Karlson, U.; Frankenberger, W. T., Jr. *Soil Sci.* **1989**, *149*, 56−61.

(11) Karlson, U.; Frankenberger, W. T., Jr. *Soil Sci. Soc. Am. J.* **1989**, *53*, 749−753.

(12) Karlson, U.; Frankenberger, W. T., Jr. *Sci. Total Environ.* **1990**, *92*, 41−54.

(13) Terry, N.; Carlson, C.; Raab, T. K.; Zayed, A. M. *J. Environ. Qual.* **1992**, *21*, 341−344.

(14) Terry, N.; Zayed, A. M. In *Selenium in the Environment*; Frankenberger, W. T., Jr., Benson, S., Eds.; Marcel Dekker Inc.: New York, 1995; pp 343−367.

(15) Thompson-Eagle, E. T.; Frankenberger, W. T., Jr. *Environ. Toxicol. Chem.* **1990**, *9*, 1453−1462.

(16) Thompson-Eagle, E. T.; Frankenberger, W. T., Jr. *J. Environ. Qual.* **1990**, *19*, 125−131.

(17) Thompson-Eagle, E. T.; Frankenberger, W. T., Jr. *Water Res.* **1991**, *25*, 231−240.

(18) Weres, O.; Jaouni, A. R.; Tsao, L. *Appl. Geochem.* **1989**, *4*, 543−563.

(19) Duckart, E. C.; Waldron, L. J.; Donner, H. E. *Soil Sci.* **1992**, *53*, 94−99.

(20) Zhang, Y. Q.; Moore, J. N. *Water, Air, Soil Pollut.* in press.

(21) Zhang, Y. Q.; Moore, J. N. *Environ. Sci. Technol.* **1996**, *30*, 2613−2619.

(22) Fio, J. L.; Fujii, R. *Soil Sci. Soc. Am. J.* **1990**, *54*, 363−369.

(23) Doran, J. W.; Alexander, M. *Soil Sci. Soc. Am. J.* **1976**, *40*, 687−690.

(24) Besser, J. M.; Huckins, J. N.; Little, E. E.; La Point, T. W. *Environ. Pollut.* **1989**, *62*, 1−12.

(25) Karlson, U.; Frankenberger, W. T., Jr. *J. Chem. Eng. Data* **1994**, *39*, 608−610.

(26) Zayed, A. M.; Terry, N. *J. Plant Physiol.* **1992**, *140*, 646−652.

(27) Karlson, U.; Frankenberger, W. T., Jr. *Soil Sci. Soc. Am. J.* **1988**, *52*, 678−681.

(28) Biggar, J. W.; Jayaweera, G. R. *Soil Sci.* **1993**, *155*, 31−36.

(29) Zieve, R.; Peterson, P. J. *Soil Biol. Biochem.* **1985**, *17*, 105−107.